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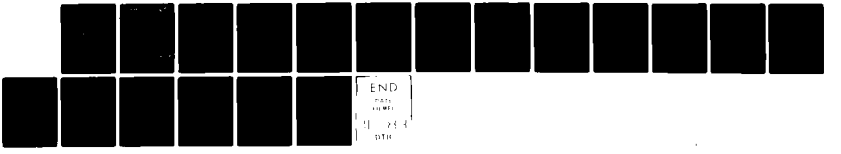

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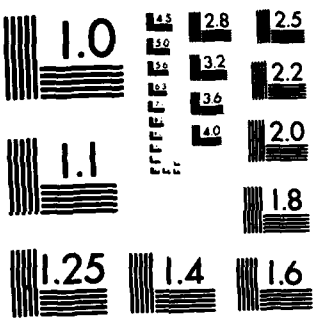

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EFFECT OF PRESSURE ON CONDUCTIVITY IN POLY(ETHYLENE OXIDE) COMPLEXED WITH ALKALI METAL SALTS

by

John J. Fontanella and Mary C. Wintersgill

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Audio frequency complex admittance measurements at a number of temperatures have been performed on PEO complexed with various alkali metal perchlorates and thiocyanates at pressures up to 0.2 GPa. In general, the activation volumes tend to increase with the size of both the cation and anion. The trend is best explained if the ion transport mechanism involves both anions and cations. The results are in good agreement with the predictions of a dynamical diffusion theory with an attempt mode Gruneisen

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EFFECT OF PRESSURE ON CONDUCTIVITY IN POLY(ETHYLENE OXIDE) COMPLEXED WITH ALKALI METAL SALTS

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Audio frequency complex admittance measurements at a number of temperatures have been performed on PEO complexed with various alkali metal perchlorates and thiocyanates at pressures up to 0.3 GPa. In general, the activation volumes tend to increase with the size of both the cation and anion. The trend is best explained if the ion transport mechanism involves both anions and cations. The results are in good agreement with the predictions of a dynamical diffusion theory with an attempt mode Gruneisen parameter appropriate for interchain vibrations. This implies that diffusion takes place via interstice-interstice hopping of the ions. Next, it is shown that free volume considerations lead to unreasonable results if T_0 is interpreted as the glass transition temperature. Finally, the effect of pressure on the activation volume is determined.

1. INTRODUCTION

Ion conducting poly(ethylene oxide)(PEO) has been attracting a great deal of attention[1-24] because of possible application as the electrolyte in solid state batteries. As the effect of pressure on the conductivity provides useful information concerning ion transport, such studies of PEO complexed with various salts were undertaken and the results are presented here.

2. EXPERIMENT AND RESULTS

Films of PEO (Polysciences, MW 5×10^6) with various amounts of alkali metal perchlorates and thiocyanates were prepared as described elsewhere.[21] As before, aluminum electrodes were evaporated onto the surfaces. One face had a central circular electrode of about 8 mm diameter while the other was about 10 mm in diameter. The samples were 0.25-0.5 mm thick. The configuration was chosen to be optimal for the apparatus used. Such a configuration does not readily yield absolute values of the conductivity at a high accuracy, however, since the primary goal of the present work is the relative change in conductance with pressure, this was considered to be a reasonable procedure.

The complex admittance measurements were made using a fully automated microprocessor-controlled bridge constructed by one of the authors (CGA). The bridge operates at five audio frequencies from 100-10,000 Hz, and is as accurate as the best commercially available manual bridges (General Radio 1616, for example).

At the relatively low temperatures of the present work, it was found that there was usually very little difference between the 1,000 and 10,000 Hz values of conductance, even though the samples were rather thin. As pressure increased, however, the apparent conductance became lower for the lower frequencies. This effect can be seen in Figure 1 where the results for PEO_8-$NaClO_4$ are shown. This is due to enhanced blocking electrode effects. However, this dispersion has little effect on the zero pressure slope, though the curvature is affected somewhat. In this paper, the 10,000 Hz data will be taken to represent the conductance of the sample.

Two different high pressure bombs were used, each with a design similar to that described elsewhere.[25] The pressures were generated using

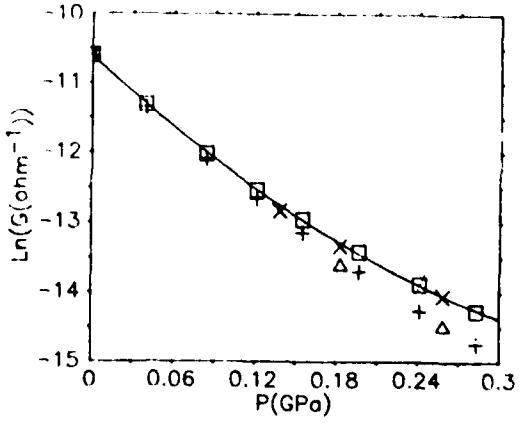

Figure 1: $\ln(G(ohm)^{-1})$ vs. P(GPa) for PEO_8-$NaClO_4$ at 314.9K. The data are: o-Increasing pressure and x-Decreasing pressure at 10,000 Hz; +-Increasing pressure and *-Decreasing pressure at 1,000 Hz. The solid line is the best fit curve for the 10,000 Hz data.

Table 1: Various experimental and theoretical results related to the effect of pressure on the ionic conductivity in PEO complexed with alkali metal salts.

Material and sample Number	T(K)	$\ln(\sigma_0(\Omega^{-1}))$	$a(GPa)^{-1}$	$b(GPa)^{-2}$	g(eV)	$v(cm^3/mol)$	γ_a	$\alpha_V(GPa)^{-1}$	α_V/γ
PEO_5-LiSCN									
1	310	-12.9	-12.4	4.5	1.13	32.3	1.27	0.72	6
1	318	-11.8	-12.6	5.8	1.13	33.7	1.31	0.91	8
PEO_8-$LiClO_4$									
1	299	-10.6	-12.0	8.1	0.76	30.3	1.77	1.3	11
1	307.2	-9.7	-14.0	16.5	0.76	36.4	2.12	2.3	19
1	315.2	-8.3	-14.5	13.1	0.76	38.6	2.25	1.8	15
2 (gas)	310.2	-9.7	-14.4	19.2	0.76	37.8	2.20	2.5	22
3	310	-9.7	-12.0	4.1	0.76	31.5	1.83	0.66	6
PEO_8-$NaClO_4$									
1	306.9	-12.1	-17.6	21.3	0.92	45.5	2.20	2.4	20
1	310.4	-11.5	-18.5	23.9	0.92	48.4	2.33	2.5	21
1	314.9	-10.6	-17.8	17.8	0.92	47.3	2.28	2.0	17
1	320.4	-9.7	-16.8	15.1	0.92	45.4	2.19	1.7	15
1	329.8	-8.2	-21.4	20.5	0.92	59.5	2.87	1.9	16
2	309.6	-11.0	-15.6	15.9	0.92	40.7	1.96	2.0	17
3	309.6	-11.8	-13.5	9.1	0.92	35.2	1.69	1.3	11
2	324.8	-8.7	-18.7	21	0.92	51.2	2.47	2.2	19
3	324.8	-9.2	-18.9	21.7	0.92	51.7	2.50	2.3	20
$PEO_{4.5}$-$NaClO_4$									
1	294.2	-11.6	-18.1	11.5	0.78	44.9	2.55	1.2	11
1	303.9	-10.5	-15.2	6.7	0.78	39.0	2.22	0.87	7
1	310.2	-10.0	-14.7	7.0	0.78	38.5	2.19	0.94	8
1	315.8	-9.3	-14.3	8.1	0.78	38.1	2.17	1.15	10
1	323.4	-8.6	-13.9	8.2	0.78	38.0	2.16	1.14	10
$PEO_{4.5}$-NaSCN									
1	310.2	-6.2	-10.0	1.7	0.41(0.76)	26.6	2.88(1.55)	0.33	3
1	318.2	-5.8	-10.6	3.2	0.41(0.76)	29.0	3.14(1.69)	0.59	5
*	321.7	-	-9.0	-	0.41(0.76)	24.9	2.70(1.45)	-	-
*	318.5	-	-9.0	-	0.41(0.76)	24.6	2.66(1.44)	-	-
$PEO_{4.5}$-KSCN									
1	310.2	-9.8	-10.7	5.0	1.10	27.9	1.13	0.92	8

*Sample provided by R. Dupon and D.F. Shriver, Northwestern University

both argon and nitrogen gases as well as Spinesstic 22 oil. The measurements of the pressure were made using a Heise 7 kbar Bourdon tube pressure gauge. In many cases, the data runs using either argon or nitrogen gas as the pressurising medium proved not to be entirely satisfactory. The samples frequently failed after one or two data runs, either by an apparent short circuit or by generating a voltage. Furthermore, the samples turned white during the pressure run. All the samples returned to their initial transparency after heating at 100C in vacuum for a few hours. Using the Spinesstic 22 as the pressure fluid, however, the samples showed no such effects and the change in appearance of the samples is therefore attributed to dissolved gas in the samples. However, the dissolved gas had very little effect on the conductivity as can be seen in Figure 2 where the results for PEO_8-$LiClO_4$ obtained using both gas and oil are shown. Clearly, the effect of pressure on the conductivity is independent of the pressurising medium. Samples removed from the pressure bomb after a week of constant immersion in the Spinesstic 22 were scrutinised for signs of swelling or chemical interaction but none showed any effects from the oil.

In interpreting the results, the equation:

$$\ln(G) = \ln(G_0) + aP + bP^2 \qquad (1)$$

where G_0, a, and b are constants, was best-fitted to the data. G is the conductance in Ω^{-1} and P is the pressure in GPa. The results of the best-fits are listed above in Table 1.

3. DISCUSSION

The data were used to calculate an activation volume associated with the conduction process. The activation volume is defined as:

$$v = \left(\frac{\partial g}{\partial P}\right)_T \qquad (2)$$

where g is the Gibbs energy. The problem is to determine the most appropriate method to associate the Gibbs energy with the ionic conductivity. The difficulty arises from the uncertainty as to whether the Arrhenius equation:

$$\sigma = \frac{\sigma_0}{T} \exp(-h/kT) \qquad (3)$$

where h is the enthalpy, or a free volume expression:

$$\sigma = \frac{\sigma_0}{T} \exp(-E_a/k(T-T_0)) \qquad (4)$$

should be used to describe the conductivity. As will be shown below, the free volume expression leads to unreasonable results and thus the Arrhenius equation will be used.

3.1. Arrhenius Analysis

The assumption of Arrhenius behavior leads to an activation volume:

$$v = -kT\left[\frac{\partial \ln \sigma}{\partial P} - \frac{\partial \ln \sigma_0}{\partial P} + \frac{1}{k}\left(\frac{\partial s}{\partial P}\right)\right] \qquad (5)$$

where the entropy, s, is given by $g = h - Ts$. Assuming that the electric field inside the sample is uniform:

$$G = \frac{A}{d} \qquad (6)$$

where A is the area of the electrodes, and d is their separation, it follows that:

$$\frac{\partial \ln \sigma}{\partial P} = \frac{\partial \ln G}{\partial P} + \frac{\kappa}{3} \qquad (7)$$

where κ is the isothermal compressibility. Further, assuming that the only pressure dependent terms in the pre-exponential are the attempt mode frequency, ν_a, the number of charge carriers per unit volume, n, and the mean squared jump distance, r, that is:

$$\sigma_0 = C\nu_a n r^2 \qquad (8)$$

and also that the entropy is independent of pressure, Equation (5) becomes:

$$v = -kT\left[\frac{\partial \ln G}{\partial P} - \gamma_a \kappa\right] \qquad (9)$$

In this expression, the attempt mode Gruneisen parameter, γ_a is given by:

$$\gamma_a = -\frac{\partial \ln \nu_a}{\partial \ln v} \qquad (10)$$

The compressibility of pure PEO is $0.117(GPa)^{-1}$ as reported by Ito.[6] As values for complexed PEO do not appear to be available at present, this value will be used for the complexed material also. There is considerable ambiguity as to the appropriate value of γ_a. Bulk Gruneisen constants for polymers are on the order of 6-10,[27] while mode Gruneisen constants range from 0.700 to about 2.28. However, the activation volume is relatively insensitive to the value of γ_a since, for $\gamma_a \kappa$ for example, the correction factor in Equation (9) ($\gamma_a \kappa$) is about $0.23(GPa)^{-1}$ which represents a difference of only about 1.% in the activation volume.

In order to be internally consistent, dynamical diffusion theory will be used to estimate γ_a. Specifically, it follows from Flynn[29] that:

$$v = -\gamma_a q \qquad (11)$$

This equation has been used successfully in similar applications for ionic crystals.[30] Inserting Equation (11) into Equation (9), the working equation becomes:

$$v = \frac{-kT\frac{\partial \ln G}{\partial P}}{1 - \frac{\kappa kT}{q}} \qquad (12)$$

The resultant values of the activation volumes are listed in the seventh column of Table 1

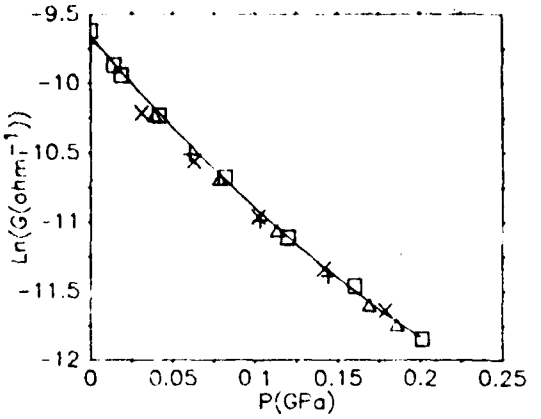

Figure 2: Ln(G(ohm)$^{-1}$) vs. P(GPa) for PEO_8-$LiClO_4$. The data are: o-Increasing pressure and x-Decreasing pressure using nitrogen gas at 310.2K; □-Increasing pressure and +-Decreasing pressure using Spinesstic 22 at 307.2K. The data are at 10,000 Hz.

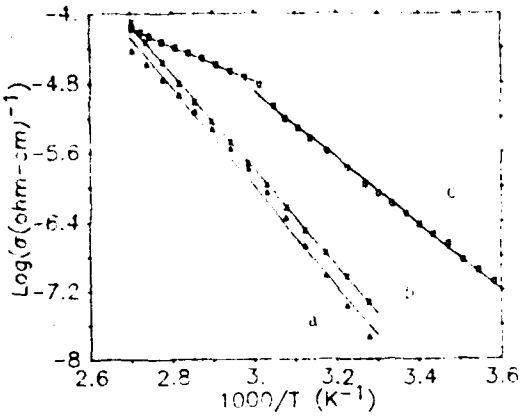

Figure 3: Ln($(ohm\text{-}cm)^{-1}$) vs. $1000/T(K^{-1})$ for PEO complexed with various alkali metal thiocyanates: (a) PEO_5-LiSCN (b) $PEO_{4.5}$-KSCN (c) $PEO_{4.5}$-NaSCN.

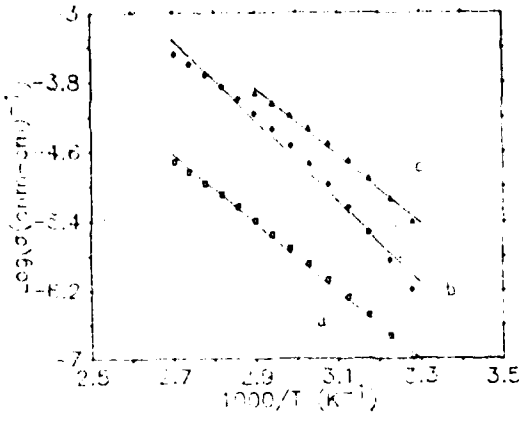

Figure 4: Ln($(ohm\text{-}cm)^{-1}$) vs. $1000/T(K^{-1})$ for PEO complexed with various alkali metal perchlorates. (a) $PEO_{4.5}$-$NaClO_4$ (b) PEO_5-$NaClO_4$ (c) PEO_5-$LiClO_4$.

using values of the Gibbs energy approximated by the enthalpies determined from the slopes in Figures 3 and 4.

There are several interesting features of these results. The most important trend is that in general the activation volume increases with both the size of the cation and anion. For example, v for $PEO_{4.5}$-$NaClO_4$ is significantly larger than that for $PEO_{4.5}$-NaSCN. The simplest explanation for this result is that the difference is due to the difference in size and shape of the anions and that the anions are mobile. That is, the tetrahedral perchlorate ion requires more volume increase of the polymer matrix than does the linear thiocyanate ion in order for transport to take place. Also, it is possible that a larger number of perchlorate ions than thiocyanate ions may be mobile. These considerations support the recent results of Weston and Steele[19,20] and Sorensen and Jacobsen[23] which imply that the anions are mobile.

Of course, other explanations are possible. For example, it is not necessary that the anions be mobile. Their function may simply be to decrease the free volume, which should in turn increase the activation volume for motion of cations. However, the difference between PEO-NaSCN and PEO-$NaClO_4$ seems to be too large to be attributable to cation motion alone. Other explanations may be associated with morphology or degree of crystallinity. Experiments are currently underway to ascertain the extent to which such factors are influencing transport processes.

Most trends shown by the remaining results are also consistent with an argument based on ion size. Specifically, the activation volume for PEO_5-$LiClO_4$ is smaller than for PEO_5-$NaClO_4$ and v for $PEO_{4.5}$-NaSCN is slightly smaller than for $PEO_{4.5}$-KSCN. The latter results are particularly significant since electrical relaxation studies show that there are severe local distortions of the polymer chains in PEO-KSCN.[21] Finally, v for PEO_5-$LiClO_4$ appears to be larger than for PEO_5-LiSCN though the difference is not so dramatic as for the sodium complexed materials.

The one clear exception to the rule of scaling of v with ion size is that v for PEO_5-LiSCN is larger than for $PEO_{4.5}$-NaSCN. However, it should be kept in mind that the LiSCN complexed materials were prepared without taking great care to exclude water and were, in fact, synthesized using hydrated LiSCN.[21] Consequently, the PEO_5-LiSCN results may be anomalous as the role of the water has yet to be determined.

Next, information concerning the transport mechanism can be obtained from further consideration of dynamical diffusion theory. In particular, the values of γ_a in Equation (11) necessary to predict the experimental values of the activation volume are of interest. These values of γ_a have been calculated and are listed in Table 1. It is seen that the values are all greater than 1.0. This implies that it is the low frequency interchain vibrations of the polymer which control the ionic motion. This is because intrachain mode Gruneisen parameters are usually much smaller, typically 0.000-0.5 while interchain γ_i's are larger than 1.0 (Ref. 28). The reason for this is simply that interchain vibrations (chain-chain) are much more strongly affected by pressure than intrachain vibrations (motions within the chain). The difference is

enhanced by the smaller frequencies which appear in the denominator of the expression for γ_{ac}, Equation 10. Consequently, the picture of ion motion in PEO suggested by the results of the present pressure work is that at high temperatures both anions and cations undergo "interstice-interstice" hopping via low frequency interchain vibrations. "Interstices" are taken to be the spaces between the polymer chains. The reason for choosing the "interstices" rather than the chains themselves as the normal sites for both anions and cations at high temperatures is that if the ions reside on the chains, the effect of pressure should be to increase the conductivity since the chains would be closer together at elevated pressures. For "interstice-interstice" jumping, increased closeness of the chains should inhibit the motion thus decreasing the conductivity, as is observed experimentally.

As an alternative transport mechanism, the intrahelical jumping process, is often discussed in conjunction with these materials, some comments here are appropriate. This process is ruled out by the large mode Grueneisen parameter as that transport mechanism would require intrachain vibrations. However, chain-end bridging, which must be associated with an intrahelical jumping process in real materials, would probably require interchain vibrations and thus such a process might be consistent with the present results. However, the conclusion that the intrahelical jumping process is not dominant in these materials is consistent with the recent results of Papke et al.[15]

3.2. Free Volume Analysis

The pressure results can also be used to comment on free volume theory as represented by Equation (4). Papke et al.[14] have shown that on the basis of a configurational entropy model Equation (4) can be derived in which:

$$E_a = kB\frac{T_0 q S_c^*}{B} \qquad (13)$$

where B is a constant, S_c^* is a configurational entropy, and T_0 is a parameter usually associated with the glass transition temperature. In order to use Equation (4) to comment on the activation volume, the first step is to consider:

$$\frac{\partial K_0}{\partial P} = \frac{S_c^*}{kB}\left[v T_0 + G\left(\frac{\partial T_0}{\partial P}\right)\right] \qquad (14)$$

assuming that S_c^* and B are independent of pressure. The two terms in Equation (14) are of approximately equal magnitude if T_0 is identified with the glass transition temperature since, for polymers in general, $(\partial T_g/\partial P)$ is about 15K/kbar[32] and for PEO, T_0 250K[19] and $v = 30$ cm^3/mol. Using these numbers, both terms in parentheses are about 12×10^{-27} K-m^3.

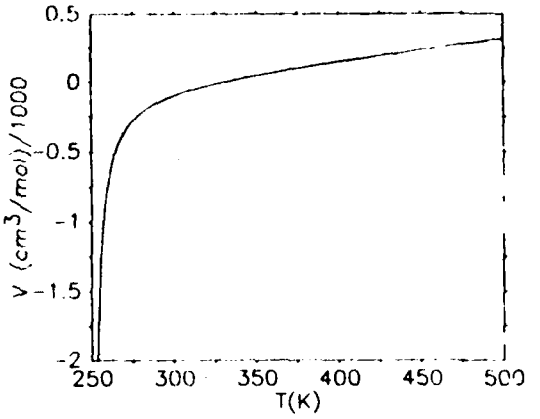

Figure 5: Activation volume vs. temperature calculated using Equation (15) and the values of the parameters given in the text.

These considerations have further implications concerning the activation volumes and the nature of T_0. It follows from Equation (4) that:

$$v = \frac{q(T-T_0)}{K_0}\left[\frac{\partial \ln \tau_0}{\partial P} - \frac{\partial \ln \tau}{\partial P}\right] + \frac{qT}{T_0(T-T_0)}\left(\frac{\partial T_0}{\partial P}\right) \qquad (15)$$

Using the same numbers as above and values of $\tau_0 = 0.5$ eV, $(\partial \ln \tau_0/\partial P) = 0$, $(\partial \ln \tau/\partial P) = 1.9$ GPa, and $K_0 = 4$ kJ/mol,[20] the values of the activation volume at various temperatures predicted by Equation (15) are plotted in Figure 5. The discontinuity at $T = T_0$ and large negative values of v for T just above T_0 are apparent. In fact, at T 320K, which is about the temperature of the present experiment, Equation (15) yields $v = -27$ cm^3/mol, a negative activation volume. As such activation volumes seem inappropriate for the present system, it is concluded that in free volume theory T_0 cannot be interpreted as the glass transition temperature.

However, it is clear that the conductivity is often non Arrhenius, obeying Equation (3)[3] and thus free volume theory is useful, though the interpretation of T_0 is unclear. An alternative interpretation is to attribute the curvature in the Arrhenius plots to "association" by analogy with ionic crystals. In PEO, association both with the chains and with each other (ion pairing) must be considered. Similar considerations have been suggested previously by Papke et al.[14] Additionally, the polymer is probably multiphase and thus some of the curvature may also be attributable to equilibration among the various phases.

3.3. Variation of v with Pressure

Finally, a few comments will be made concerning the curvature of the ln(G) vs. pressure plots. The values of b in Equation (1) range from about 2 to 20(GPa)$^{-1}$. These values are not unphysical as can be seen from the following analysis. Ignoring the correction term in Equation (9), the "compressibility of the activation volume," κ_V, can be calculated from:

$$\kappa_V = -\frac{d\ln v}{dP} = \frac{2kTb}{v} \qquad (16)$$

The results of the calculations are listed in Table 1. It is seen that the compressibility of the activation volume range from about 3 to 22. This agrees with the theoretical expectations[33-35] and the experimental results[30] in ionic crystals where the compressibility of the migration volume is found to be on the order of 5-25 times the compressibility of the host lattice.

4. SUMMARY

In summary, the effect of pressure on the ionic conductivity in alkali metal perchlorate and thiocyanate complexed PEO has been measured. The primary results are as follows.

(a) The activation volume scales with the size of both the anion and the cation. The simplest explanation of this is that both the anions and cations are mobile.

(b) The experimental results for the activation volume are in good agreement with the predictions of a dynamical diffusion theory with an effective mode Grüneisen parameter of about 2. This implies that the motion of the ions is governed by intrachain vibrations thus favoring intersite-intersite hopping of the ions.

(c) Free volume analysis lead to a negative activation volume if T_o is interpreted as the glass transition temperature. Consequently, curvature in the Arrhenius plots may better be interpreted in terms of "association" of the ions with the chains or with each other. In addition, crystallization of a multiphase system will also be considered.

(d) The compressibility of the activation volume is found to be about an order of magnitude larger than the compressibility of the host polymer.

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REFERENCES

*On leave from Simon Bolivar University, Caracas, Venezuela

[1] Fenton, D.E., Parker, J.M., and Wright, P.V., Polymer 14 (1973) 589.
[2] Wright, P.V., Br. Polymer J., 7 (1975) 319.
[3] Wright, P.V., J. Polymer Sci.: Polymer Phys. 14 (1976) 955.
[4] Parker, J.M., Wright, P.V., and Lee, C.C., Polymer, 22 (1981) 1305.
[5] Lee, C.C. and Wright, P.V., Polymer, 23 (1982) 681.
[6] Payne, D.R. and Wright, P.V., Polymer, 23 (1982) 690.
[7] Archer, W.I. and Armstrong, R.D., Electrochemica Acta, 25 (1980) 1677.
[8] Archer, W.I. and Armstrong, R.D., Electrochemica Acta, 25 (1980) 1673.
[9] Dupon, R., Whittmore, D.H., and Shriver, D.F., J. Electrochem. Soc., 128 (1981) 715
[10] Papke, B.L., Ratner, M.A., and Shriver, D.F., J. Phys. Chem. Solids, 42 (1981) 493.
[11] Papke, B.L., Dupon, R, Ratner, M.A., and Shriver, D.F., Solid State Ionics, 5 (1981) 685.
[12] Shriver, D.F., Papke, B.L., Ratner, M.A., Dupon, R., Wong, T., and Brodwin, M., Solid State Ionics, 5 (1981) 83.
[13] Papke, B.L., Ratner, M.A., and Shriver, D.F., J. Electrochem. Soc., 129 (1982) 1434.
[14] Papke, B.L., Ratner, M.A., and Shriver, D.F., J. Electrochem. Soc., 129 (1982) 1694.
[15] Dupon, R., Papke, B.L., Ratner, M.A., Whittmore, D.H., and Shriver, D.F., J. Am. Chem. Soc., 103 (1982) 6022.
[16] Armand, M.B., Chabagno, J.M., and Duclot, M.J., in Fast Ion Transport in Solids, eds Vashishta, P., Mundy J.N., and Shenoy, G.K., (North Holland, Amsterdam, 1979) p. 131.
[17] Tancella, R.J., Bailey, W., Fredrich, D., and Story, H.S., Solid State Ionics, 5 (1981) 663.
[18] Weston, J.E. and Steele, B.C.H., Solid State Ionics, 2 (1981) 347.
[19] Weston, J.E. and Steele, B.C.H., Solid State Ionics, 7 (1982) 75.
[20] Weston, J.E. and Steele, B.C.H., Solid State Ionics, 7 (1982) 81.
[21] Fontanella, J.J., Wintersgill, M.C., Calame, J.P., Andeen, C.G., Solid State Ionics, to be published.
[22] Wintersgill, M.C., Fontanella, J.J., Calame, J.P., Figueroa, J.R., Andeen, C.G. Solid State Ionics, submitted.
[23] Sorensen, P.R. and Jacobsen, T., Electrochemica Acta, 27 (1982) 1671.
[24] Sorensen, P.R. and Jacobsen, T., Polymer Bulletin, 9 (1983) 47.
[25] Fontanella, J., Andeen, C., and Schuele, D., Phys. Rev. B6 (1972) 582.
[26] Yoo, I., in High Pressure Science and Technology, 1979 Kiamesha conference, Vol.1, Physical Properties and Techniques, Ed. Timmerhaus, K.D. and Barber, M.S., (Plenum

[27] Broadhurst, M.G. and Mopsik, F.I., J. Chem. Phys., 52 (1970) 3634.
[28] Wu, C.K., Jura, G, and Shen, M., J. Appl. Phys., 43 (1972) 4348.
[29] Flynn, C.P., Point Defects and Diffusion, (Oxford: Clarendon, 1972).
[30] Fontanella, J.J., Wintersgill, M.C., Chadwick, A.V., Saghafian, H., and Andeen, C.G., J. Phys. C: Solid State Phys., 14 (1981) 2451.
[31] Zallen, R., Phys. Rev. B4 (1971) 4335.
[32] Quested, D.L. and O'Keeffe-Lanzi, M., J. Appl. Phys. 53 (1982) 6677.
[33] Varotsos, P.A., J. Physique Lett. 38 (1977) L-455.
[34] Varotsos, P.A., Phys. Rev. B18 (1978) 2683.
[35] Varotsos, P and Alexopoulos, K., Phys. Stat. Sol. (a)47 (1978) K133.

NOTE ADDED IN PROOF

After the completion of the work described above, two experiments were performed which extend and support the results reported above. First, careful differential scanning calorimeter (DSC) measurements were performed on all samples using a DuPont 990 DSC. The data for $PEO_{4.5}$-$NaClO_4$ and $PEO_{4.5}$-NaSCN were extremely similar consisting of a weak, narrow melting at low temperatures (20-30C), a stong, narrow melting at high temperatures (150-180C), and a weak, broad endothermic event between these two peaks. This supports the comparison of these two materials at all temperatures. That data will be presented in detail elsewhere.

Second, the temperature range of the pressure measurements was extended to 350K for the two most important materials, $PEO_{4.5}$-$NaClO_4$ and $PEO_{4.5}$-NaSCN. The results for $PEO_{4.5}$-$NaClO_4$ can be represented by:

$$\ln(G(\Omega^{-1})) = -7.9 - 10.2P + 4.6P^2$$

and

$$\ln(G(\Omega^{-1})) = -8.0 - 7.3P$$

describes the data for $PEO_{4.5}$-NaSCN. The latter material was a hot-pressed sample provided by Northwestern University while the former was a film prepared in our laboratory. These results lead to activation volumes of 30.2 and 22.0 cm^3/mol, respectively. Once again, the activation volume for $PEO_{4.5}$-$NaClO_4$ is found to be much larger than for $PEO_{4.5}$-NaSCN. Consequently, this extends and supports the arguments above concerning ion size effects on γ and the resultant conconclusion concerning anion motion in these materials. Next, the activation volumes are smaller at 350K than at lower temperatures though not small enough to change any of the arguments presented above concerning the transport mechanism. That is, since γ_a=1.72 and 2.38(1.29) for these materials at 350K, these are still much larger than would be expected for intrachain mode gammas. Finally, it is noted that the extremely large decrease in v (26.4 to 15.9 cm^3/mol for 313 to 350K) as temperature increases which is reported by Chadwick, Strange, and Worboys for $PEO_{4.5}$-NaSCN at this conference, is not reproduced in the present work. However, it is noted that the $PEO_{4.5}$-NaSCN studied at 350K in the present

work was hot-pressed while that of Chadwick et al. was a film. Consequently, some of the difference may be due to the difference between the preparative techniques. In support of this, the $PEO_{4.5}$-NaSCN films studied in the present work showed significant curvature while the hot-pressed samples did not. Further, the zero pressure slope for the hot-pressed sample is about 10% lower than for the film. In addition, the $PEO_{4.5}$-$NaClO_4$, which is a film, does exhibit a somewhat larger decrease in activation volume as temperature increases (38.5 to 30.2 cm^3/mol for 310 to 350K) than does the hot-pressed $PEO_{4.5}$-NaSCN. However, the decrease is still much smaller than that observed by Chadwick et al. Whatever the magnitude, it is clear that v does decrease with increasing temperature. Some decrease is expected since, as temperature increases and the polymer expands, the free volume increases and thus the activation volume should decrease. However, the decrease in activation volume appears to be too large to be explained by this effect. Rather, these results may represent evidence for an "association" process occurring in the polymer. In such a model, the large decrease in activation volume follows since at low temperatures there is a "volume of formation" for the associated ions in addition to a "motion volume." The activation volume then decreases because the "formation volume" decreases due to increased "dissociation" as temperature increases.

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